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(54) **The incorporation of additives into polyesters.**

(57) The addition of additives, in particular colourants, to polyesters such as polyethyleneterephthalate is achieved by dissolving or dispersing the additive into an ester of an alcohol and a substantially straight chained fatty acid having from C_{14}-C_{22} carbon atoms.

The advent of a liquid colourant has particular advantages to the food packaging industry.

The preferred carrier is the ester of oleic acid and ethylene glycol and thus may additionally comprise a thickener or a plasticiser.

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The present invention relates to the incorporation of additives into polyesters, and more particularly, though not exclusively, to the incorporation of colourants into esters of aromatic di-acids, such as, for example polyethyleneterephthalate (PET), polybutyleneterephthalate (PBT) and polyethyleneterephthalateglycol (PETG), which results where cyclohexanedimethanol is used to reduce the reaction times in esterification of ethyleneglycol and terephthalic acid.

More particularly still, the invention is concerned with providing liquid colourants for colouring polyesters which are used in the packaging of food and drink.

One aspect of the invention provides a liquid colourant for colouring polyesters in the following manufacturing processes, namely the production of coloured polyester sheets or film by extrusion, the production of polyester mouldings by injection moulding and the production of coloured polyester bottles by extrusion blow moulding and injection blow moulding.

It is known to incorporate additives into polymers. Depending on the polymer, additives can be incorporated using a variety of techniques.

Colourants, for example, may be compounded with the natural polymer at the required use level and moulded as such.

However, the compounded route is expensive and only feasible for large tonnages. It also suffers the disadvantage that long lead times are required and large volumes of stock are needed for each colour; this means space is tied up and working capital is absorbed.

It is more usual to produce "master batches" by compounding the colourant with the polymer. This involves mixing dry pigment or dye into the polymer at a higher than normal percentage and extruding. The resultant master batch of concentrate is granulated and sold to moulders. These master batches are then blended with the natural polymer at the machine to give coloured mouldings. The disadvantage with such methods is that uneven dispersion of the dye within the master batch often results in poor dispersion of the dye in the melt compounding process.

Alternatively, the additive may be introduced into the polymer in liquid form by dispersing the additive in an appropriate carrier. Using liquid carriers is particularly favoured when the additive is a colourant, since liquid colourants have the following advantages over the use of dry pigments and concentrates, namely:

(a) Liquid colourants can be dosed into a moulding machine just below the hopper whereas with dry pigments and concentrates an in-hopper mixer is normally required. With liquid colourants a thorough mixing of the liquid colourant with the natural polymer can be effected by the plasticising screw.

(b) The dosage of liquid colourants can be very accurately controlled using self sensing peristaltic pumps. These adjust themselves to give the correct injection of liquid at each cycle.

(c) Liquid colourant dose rates vary from 0.1% to 2% which are small compared to solid systems. It is therefore much cheaper to colour by the liquid route, and

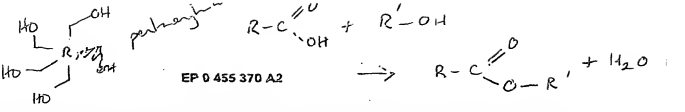
(d) With a liquid system the colour change can be effected by removing a tube of one colour from the throat area of the equipment and substituting it with one of the next colour; no cleaning is required. On the other hand, with solid systems colour change is a very time consuming process since the coloured material must be completely removed from the large heated hopper assembly needed to deliver the polymer in a completely dry condition.

Whilst liquid systems have been developed for use with the polyolefins such as polypropylene, polystyrene and polyethylene, these liquid colourants comprise a variety of plasticisers, surfactants and suspending agents which have proved to be unsuitable with, polyesters such as for example, PET,PETG and PBT

The production of liquid colourants for use with those polyesters used in the food industry, for example PET, PETG and PBT has not hitherto been possible due to the critical requirements of these polymers and food contact regulation requirements. In particular, the viscosity and clarity of these polymers is significantly affected by the introduction of foreign additives. Furthermore, water must be excluded as it breaks the ester bonds of the polymer at standard moulding conditions. It is therefore vital that any additives or carrier added to the polymers do not noticeably affect the physical properties.

The liquid colourants used with more tolerant polymers, such as, for example polyethylene and polystyrene proved incompatible with, polyesters for example, PET, PETG and PBT. Their use resulted in cloudy mouldings. This was probably due to significant quantities of water being present. (An aqueous content of greater than 5 parts per million was found to result in de-esterification of the polyester with a resultant loss of physical strength and clarity). Furthermore, if the polyester, such as, for example, PET, PETG and PBT was coated with a polyvinylidenedichloride (PVdC) layer to reduce oxygen permeability, essential for storing beer and cider, the liquid systems would migrate under pressure through the PET, PETG or PBT causing bubbles to appear under the PVdC coating.

U.S. 4 443 573 discloses dispersions and a process for their incorporation into fibre forming polymers. The dispersions comprise a polymer additive and a carrier of pentaerythritol or dipentaerythritol and a fatty acid of



C_5 through C_{26}. In particular the invention is concerned with adding titanium dioxide to polyamides and polyesters to decrease the lustre of the resulting spun fibre. The examples refer to the use of esters of C_5-C_{10} fatty acids and all incorporate wetting agents.

It is an object of the present invention to provide a means of introducing additives, and in particular colourants, via a liquid route into polyesters such as for example those derived from ethylene glycols and terephthalic acids, more particularly PET, PBT and PETG.

According to one aspect of the present invention there is provided an additive-containing composition for introducing said additive into polyesters, said composition comprising an additive dissolved or dispersed in a a liquid carrier, characterised in that the liquid carrier comprises an ester of a C_{14}-C_{22} fatty acid and an alcohol.

Preferably the C_{14}-C_{22} fatty acids are substantially unbranched hydrocarbons. The alkyl chain may be saturated or it may contain one or more double bonds. Where there are several double bonds present these will be separated by at least one methylene group.

The fatty acid is preferably a liquid-at room temperature and will therefore include the unsaturated fatty acids derived from myristate, palmitate, stearate, arachidate and behenate. Examples of those derivatives with one double bond include palmitoleate and oleate, those with two double bonds include linoleate, those with three double bonds include linolenate and those with fourinclude arachidonate. Only those which give rise to a liquid ester on reaction with an alcohol will however be suitable.

Generally speaking, as the chain length of the fatty acid decreases and the number of double bonds increases, the fluidity of the fatty acid will increase, and the fatty acids will become more suitable.

Short chain fatty acids are likely to be too volatile and long chain fatty acids will be solid depending of cours on the degree of saturation, since the more saturated the fatty acid, the more likely it is to be solid.

Thus the preferred, fatty acids from which the ester of the invention may be derived, will be the C_{18} to C_{20} fatty acids and more preferably still oleic acid.

Fatty acids are often obtained commercially as products from natural sources and may therefor contain a number of impurities. For example oleic acid, may be a mixture of 67% C_{18-1} oleic acid with C_{18-2} linoleate, C_{16-0} stearate and C_{16}, C_{14} and C_{20} homologues of these. Thus the fatty acid of choice is in practice likely to be a substantially unsaturated fatty acid of a given type but containing other derivatives.

The esters of fatty acids in the C_{14}-C_{22} range are particularly desirable since they also act as wetting agents, thereby aiding dispersion. As a result colourants and other additives can be introduced in far greater amounts that is possible with esters of fatty acids in the C_5-C_{10} range. This is particularly desirable where opaque colouration is required.

Comparative tests on C_5-C_{10} esters of pentaerythritol and a C_{18-1} ester indicated a 33% increase in th loading of TiO_2 could be achieved with the C_{18-1} ester.

Furthermore flocculation of the additive was exhibited when the C_5-C_{10} esters were mixed with a polymer melt. As well as giving rise to an unacceptable appearance, this effect indicates incompatibility and therefore unsuitability where the products are to be associated with food products.

Similarly the higher chained fatty acids such as C_{28} are solid at room temperature and are therefore unsuitable.

The preferred alcohols from which the ester of the invention are derived are polyols, preferably a polyhydroxyalkyl which may be straight and/or branched and which will have a number of hydroxy groups available for ester formation with the fatty acids.

Preferably the alcohol will have at least 3 hydroxy groups such as, for example, trihydric alcohols such as glycerol $C_3H_5(OH)_3$. More preferably however, the alcohol will have at least 4 hydroxy groups and will include compounds such as, for example, pentaerythritol and tetraethylolmethane.

The ester resulting from reacting the aforementioned acids and alcohols will then be used to introduce additive, preferably colourants into polyesters of the type described.

However additives other than colourants may be mixed with the carrier, and these may include plasticisers, preferably an adipic acid or a phthalic acid ester of a C_6-C_{15} alcohol, for example di 2-ethylhexyl ester, most preferably di 2-ethylhexyl adipate DEHA or diisodecyl adipate DIDA. These ester plasticisers enable the highest possible load of colourant to be obtained.

Preferably the fatty acid is a monounsaturated fatty acid such as oleic acid and the alcohol is pentaerythritol; the resulting ester is more preferably the mono, di or tri oleate, more preferably still the dioleate.

In one embodiment the additive is a colourant, and since these are the additives most commonly introduced into polyesters, for example those formed from reacting ethyleneglycol and terephthalic acid, most commonly PET or PETG, the invention will be described with reference to the introduction of colourants into these polymers although it will be understood by one skilled in the art that it is not restricted to the introduction of colourants into these specific polymers.

One advantage of the invention is that the carrier acts as a wetting agent. It can therefore carry more additives than other carriers.

According to another aspect of the invention there is provided an additive containing composition for introducing said additive into polyesters, said composition consisting essentially an additive dissolved or dispersed in a liquid carrier, characterised in that the liquid carrier consists of an ester of a C_{14}-C_{22} fatty acid and alcohol.

The carrier pentaerythritol oleate is particularly suitable for use in the food industry, since it is not toxic and has been found not to migrate above detectable limits making it particularly suitable for introducing colourants into polyesters which are used in the manufacture of food packaging.

According to a further aspect of the invention there is provided a method of producing coloured polyester bottles by the addition of a colourant into a process, characterised in that said colourant is added as a liquid comprising the colourant and pentaerythritol oleate.

According to a further aspect of the invention there is provided a method of producing coloured polyester sheet or film by the addition of a colourant in a process, characterised in that said colourant is added as a liquid comprising the colourant and pentaerythritol oleate.

According to a further aspect of the invention there is provided a method of producing coloured polyester mouldings by the addition of a colourant in a process, characterised in that said colourant is added as a liquid comprising the colourant and pentaerythritol oleate.

In one embodiment pentaerithritol oleate, in the form pentaerythritol di-oleate (although any of the oleate forms or combinations thereof may be used) is present in amounts from 10% to 98% by weight of the total weight of composition.

The liquid colourants will contain a minimal water content, preferably less than 5 parts per million, and will have low volatility at the temperature of use (260°C - 320°C).

Since in one embodiment the compositions are to be used to colour plastics used in bottle making and the bottles are likely to contain beverages and cosmetics, it is essential that the colourant and carrier are of very low toxicity and are used in amounts which in the final product do not migrate above prescribed limits.

The composition may contain other additives including emulsifiers and surface active agents, such as, e.g. polyoxyethylene derivatives of fatty acid partial esters of sorbitol anhydride, for example Tween 80, wetting agents, and ester plasticisers, for example di 2-ethylhexyl adipate (DEHA), di-isodecyl adipate (DIDA) di(iso) octyl phthalate (D(I)OP) and di(2-ethylhexyl) phthalate (DEHP).

Preferably the additives are used in the following ranges:

Pentaerythritol oleate (carrier)	10 - 98% by weight
Colourant (additive)	2 - 90%
Ester plasticiser	0 - 10%
Wetting agent	0 - 1%
Desiccant	0 - 1%
Emulsifier/surface active agent	0 - 10%
Rheological control agent	0 - 2%

According to a further aspect of the present invention there is provided a method of introducing an additive into a polyester, the method comprising dissolving or dispersing the additive into an ester of a fatty acid and an alcohol and introducing the resulting liquid into the polyester characterised in that the ester is of a C_{14}-C_{22} fatty acid.

In one embodiment the additive, a colouring agent, is dispersed in pentaerythritol oleate and the resulting dispersion is used to colour PET, PBT or PETG.

In one embodiment a plasticiser is added. This has the advantage that loading of the colourant can be further increased. This is particularly desirable where opaque colours are required. The plasticiser acts to reduce the viscosity, thereby increasing the load.

In another embodiment, a thickener is added. This has the advantage of decreasing the load of the colourant and is particularly desirable where tints are required.

The invention will be further described by way of example only with reference to the following example compositions. These were all prepared by high speed stirring using a Cowles-type blade. Pigment dispersions as distinct from dyes were subsequently milled to ensure full wetting and deagglomeration.

EXAMPLE 1

In order to colour a PET bottle green, a liquid colourant, which could be added to PET was prepared. The liquid colourant comprised the following composition:

TRANSPARENT GREEN

P.E.Dioleate	55.00 %
Solv. Green 28	45.00 %

(Solvaperm Green G Hoechst)

The composition was added to PET in sufficient quantity to produce the desired colour.

For other colours, compositions comprising components in the following proportions may be used:

EXAMPLE 2

TRANSPARENT BLUE

P.E. Dioleate	50.00%
Solv. Blue 35	50.00%

(Waxoline Blue RPFW, ICI)

EXAMPLE 3

TRANSPARENT VIOLET

P.E. Dioleate	47.00%
Solv. Vl. 17	53.00%

(Waxoline Violet AFW, ICI)

EXAMPLE 4

BROWN

P.E. Dioleate	33.00%
Red Iron Oxide	67.00%

(Bayferrox 120NM Bayer

EXAMPLE 5

WHITE

P.E.Dioleate	40.00%
TiO_2 (Plastics Grade)	60.00%

The compositions can be made very pale by using very little colourant compared to carrier, although it will probably be necessary to add a thickener. Thus, for example, when making a pale blue sample match a composition of the type given in Example 6 may be prepared.

EXAMPLE 6

P.E. Dioleate	92.12%
hydrogenated castor oil	1.88%
Solvent Violet 17 base	3%

Solvent Blue 35 base 3%

It will be noted that the preferred thickener is hydrogenated castor oil, although other thickeners could be used.

Other additives, for example, may include: general purpose emulsifiers and surface active agents, e.g. polyoxyethylene derivatives of fatty acid partial esters of sorbitol anhydride such as Tween 80; plasticisers such as DEHA, DOP, DIOP and DIDA; wetting agents, and desiccants.

Thus for example a straight white PET colouring composition may comprise the components given in Example 7 or 8 which have higher pigment loadings than Example 5.

EXAMPLE 7

STRAIGHT WHITE

P.E. Dioleate	19.8 %
TiO_2 (Plastics Grade)	67.0 %
DEHA.	13.2 %

EXAMPLE 8

STRAIGHT WHITE

P.E. Dioleate	10.00%
Tween 80 (ICI)	6.00%
DEHA.	8.85%
TiO_2 (Plastics Grade)	74.44%
Wetting Agent	0.5%
Desiccant	0.56%

Claims

1. An additive-containing composition for introducing said additive into polyesters, said composition comprising an additive dissolved or dispersed in a liquid carrier, characterised in that the liquid carrier comprises an ester of a C_{14}-C_{22} fatty acid and alcohol.

2. A composition as claimed in claim 1, in which the fatty acid is at least a monounsaturated unbranched hydrocarbon.

3. A composition as claimed in claim 1 or 2, in which the fatty acid is oleate.

4. A composition as claimed in any of the preceding claims, in which the alcohol is a polyol having at least 3 hydroxyl groups.

5. A composition as claimed in any of the preceding claims, in which the alcohol is pentaerythritol.

6. A composition as claimed in any of the preceding claims, in which the ester is pentaerythritol oleate.

7. A composition as claimed in claim 6, in which the pentaerythritol oleate is pentaerythritol dioleate.

8. A composition as claimed in any of the preceding claims, wherein the additive is a colourant.

9. A composition as claimed in any of the preceding claims, which further comprises a plasticiser.

10. A composition as claimed in claim 9, in which the plasticiser is adipic acid or a phthalic acid ester of a C_8-C_{12} alcohol.

11. A composition as claimed in claim 9 or 10, in which the plasticiser is DEHA or DIDA.

12. A composition as claimed in any of the preceding claims, which further comprises a thickener.

13. A composition as claimed in claim 12, in which the thickener is hydrogenated castor oil.

14. An additive-containing composition for introducing said additive into polyesters, said composition consisting essentially an additive dissolved or dispersed in a liquid carrier, characterised in that the liquid carrier consists of an ester of a C_{14}-C_{22} fatty acid and alcohol.

15. A method of producing coloured polyester bottles by the addition of a colourant into a process, characterised in that said colourant is added as a liquid in a composition as claimed in claim 8.

16. A method of producing coloured polyester sheet or film by the addition of a colourant in a process, characterised in that said colourant is added as a liquid in a compostion as claimed in claim 8.

17. A method of producing coloured polyester mouldings by the addition of a colourant into a process, characterised in that said colourant is added as a liquid in a composition as claimed in claim 8.

18. A method of introducing an additive into a polyester, the method comprising dissolving or dispersing the additive into an ester of a fatty acid and an alcohol and introducing the resulting liquid into the polyester, characterised in that the ester is of a C_{14}-C_{22} fatty acid.

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